

Hyphenated Techniques for Determining pH Dependent Pore-Scale Uranium (VI) Speciation: FFF-ICP-MS

PIs

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Talk Outline

- Introduction
 - Project relevance
 - Aqueous speciation
- Field Flow Fractionation
 - Theory & instrumentation
 - Application for U characterization (previous work)
 - Laboratory bacteria U sorption
 - SREL soil leachate
 - Aquitard pore water
 - Quantitative application for U speciation
 - Well-defined ligands
- Future work

INTRODUCTION: Project Relevance

U.S. Department of Energy
Office of Science

Office of Biological and Environmental Research
Environmental Remediation Sciences Division

ENVIRONMENTAL SCIENCES PE

Providing the scientific

3. Develop new
monitoring to
manage contaminant
approaches for
chemical and
natural environ

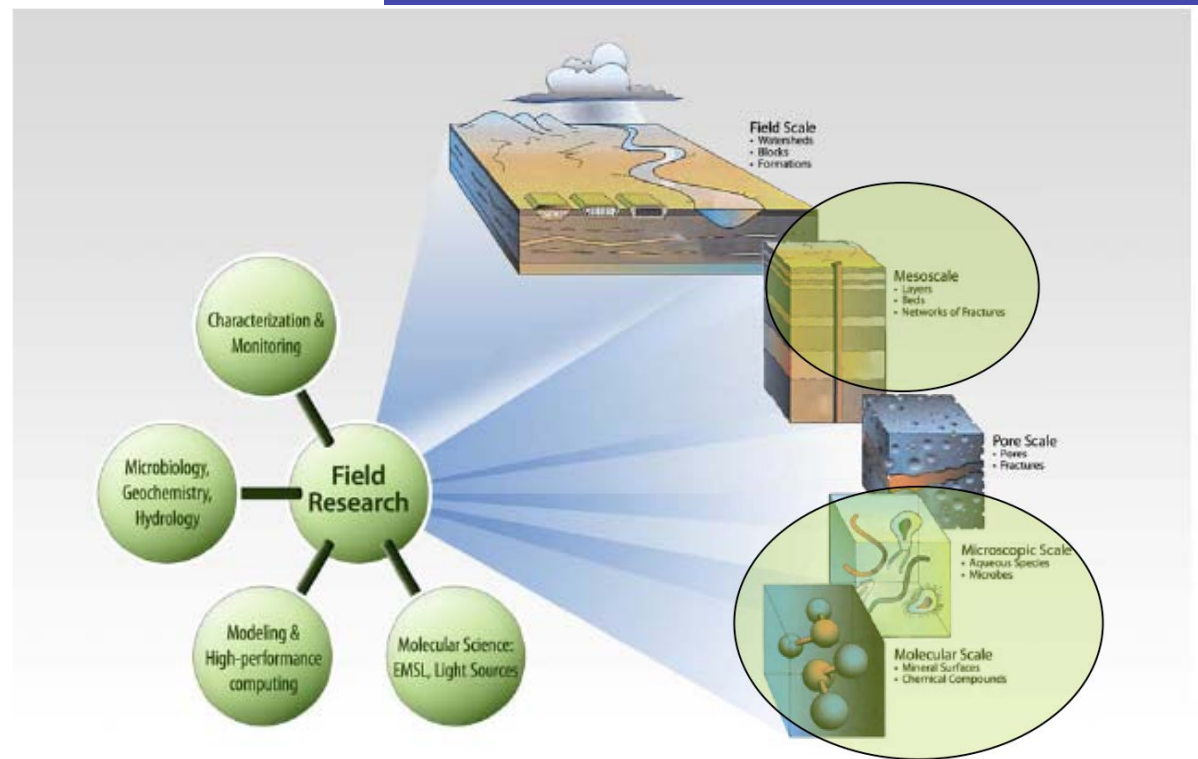
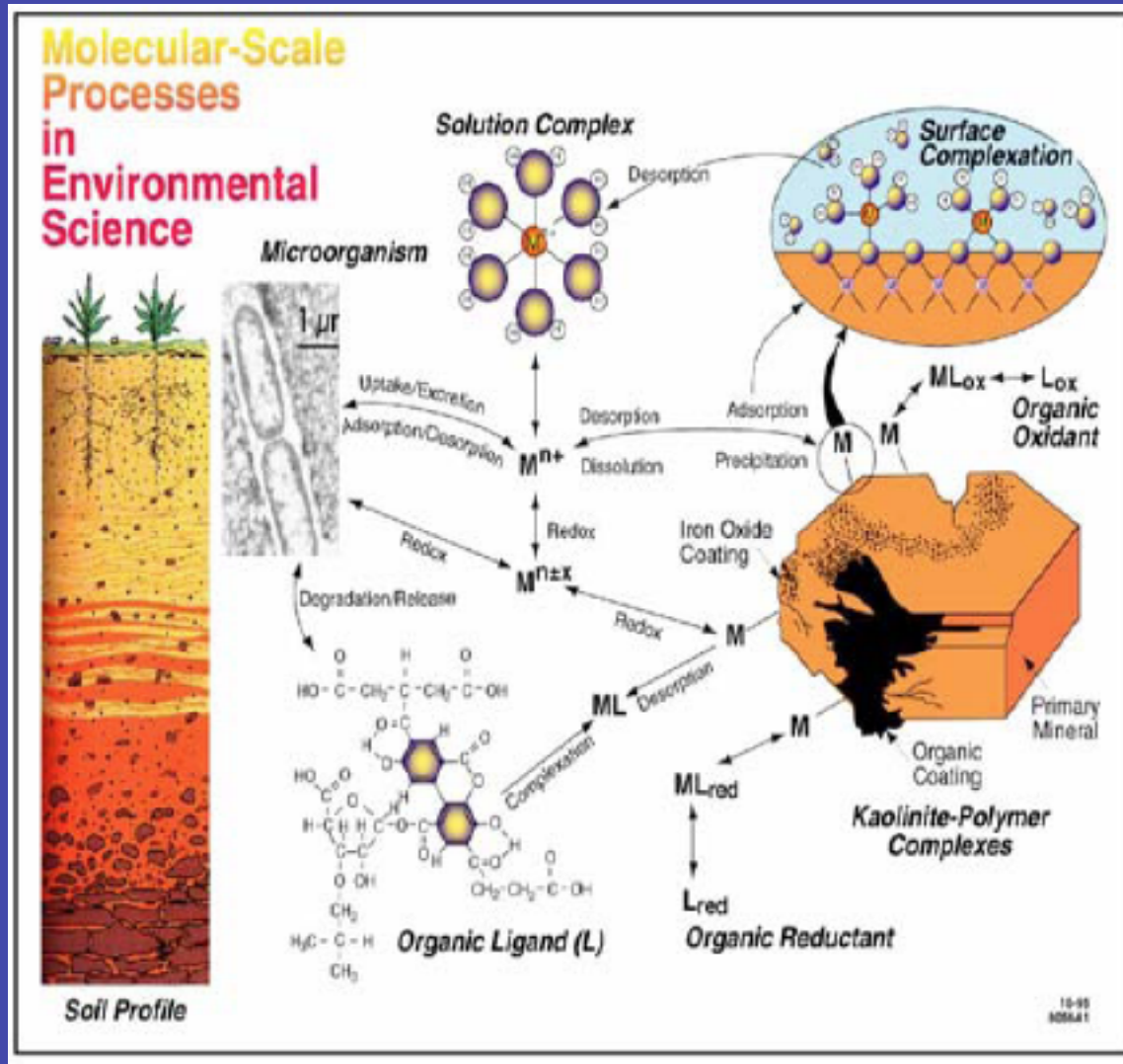


Figure 1. DOE's remediation challenges occur in the field where highly interactive natural processes occur over a broad range of scales control the fate and transport of contaminants. The ERSD goal is to help provide the basis for development of innovative remediation measures and to support decision making critical to long-term site stewardship.

INTRODUCTION:Project Hypotheses

- Geochemical
 - Uranium solution speciation in groundwater will depend on solution composition and will respond to changes in composition
 - Geochemical process such as sorption and biotransformation will be affected by U speciation
- Analytical
 - Hyphenated techniques that combine separation (field flow fractionation) and detection (ICP-MS) can provide a means of speciation measurement
 - Developed techniques, which utilize small volume samples (micro liter), will allow examination of U solution phase speciation with high spatial resolution in heterogeneous systems

INTRODUCTION: Speciation



Stanford Environmental Molecular Science Institute (EMSI)

Studying chemical and microbial interactions at environmental interfaces

Solution
Speciation
Influences
Contaminant
Behavior

Complex
formation with
aqueous and
surface ligands

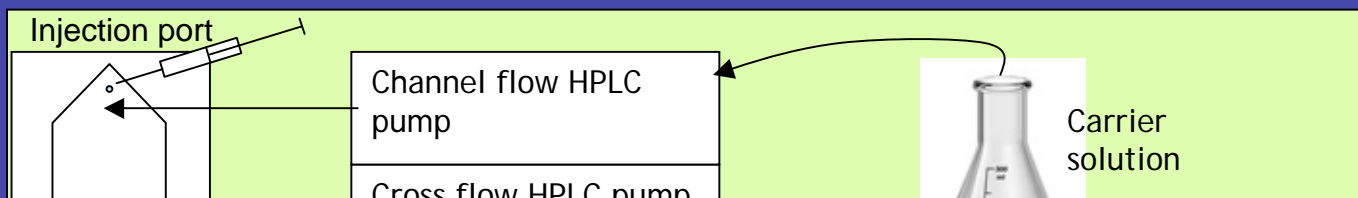
Macromolecular,
nanoparticulate,
and colloidal
ligands

Field flow fractionation Theory & Instrumentation

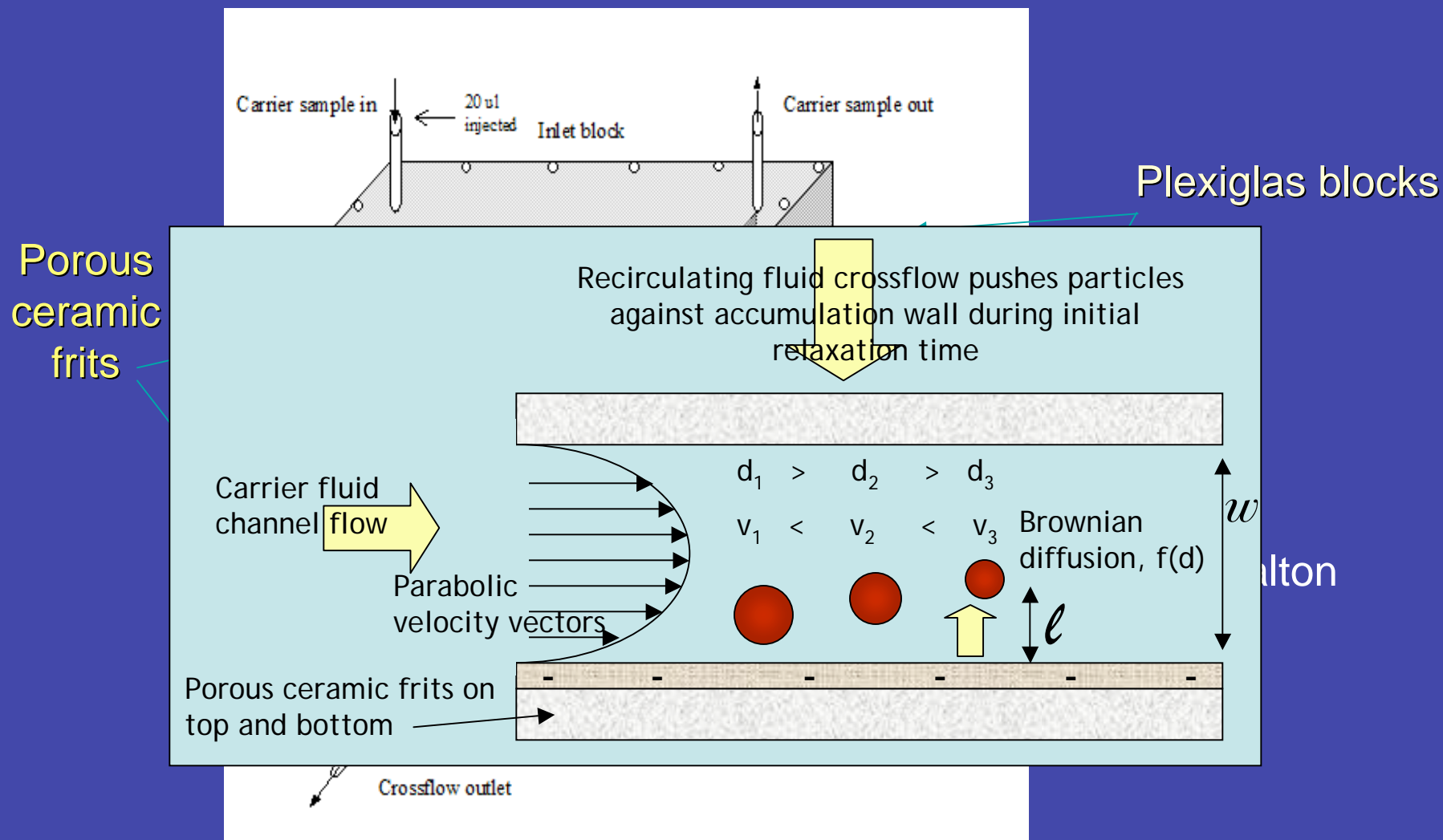
FFF is a separation method that when combined (hyphenated) with ICP-MS will allow measurement of aqueous phase U(VI) speciation

Analogous to chromatography
(no stationary phase)

Field flow fractionation - ICP-MS

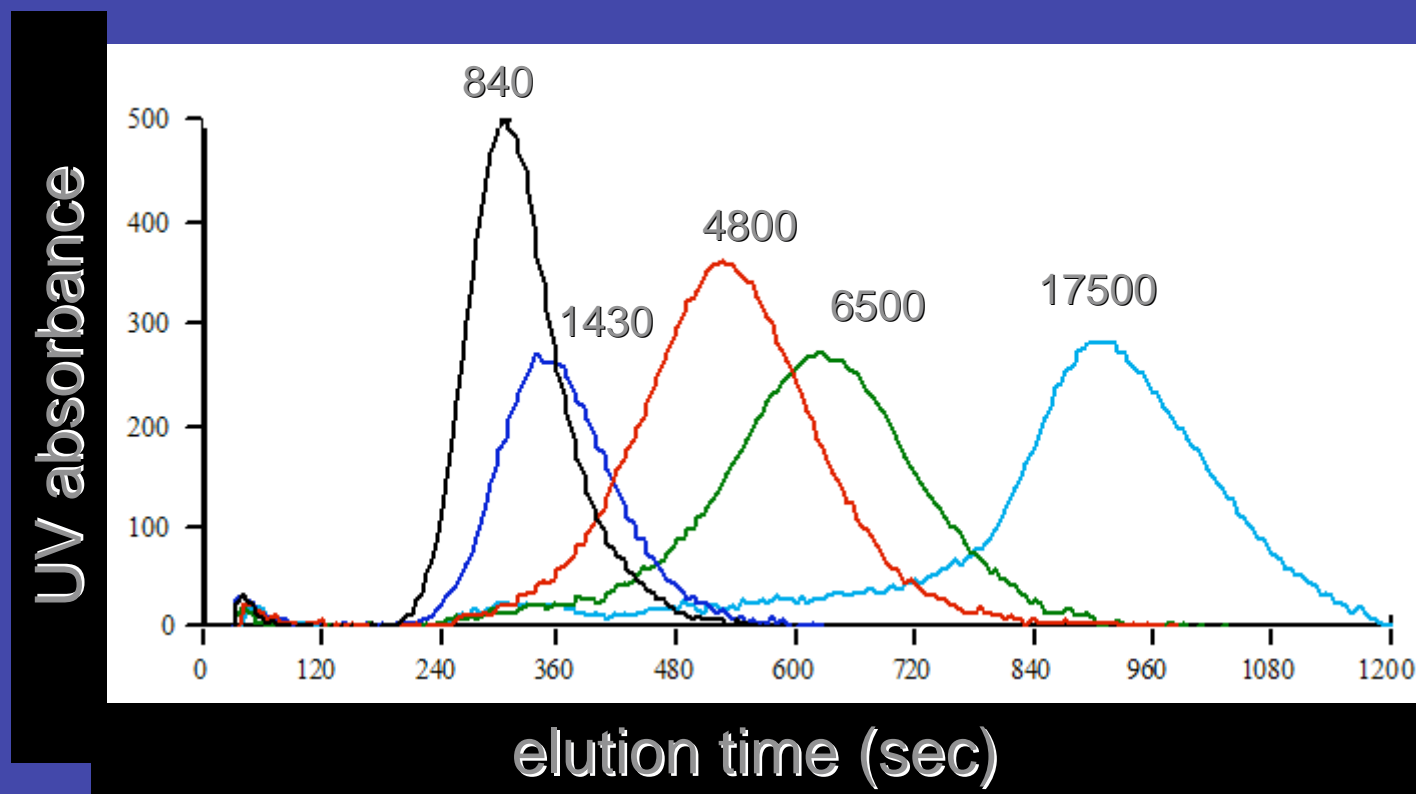


Flow FFF: Channel Configuration



- Separates colloids (inorganic or organic solids from ~ 2 nm – 1μ m size range)
- Supra-micron particles can also be analyzed using alternate FI FFF modes (1-20 μ m)

High field FI FFF for separation of DOC

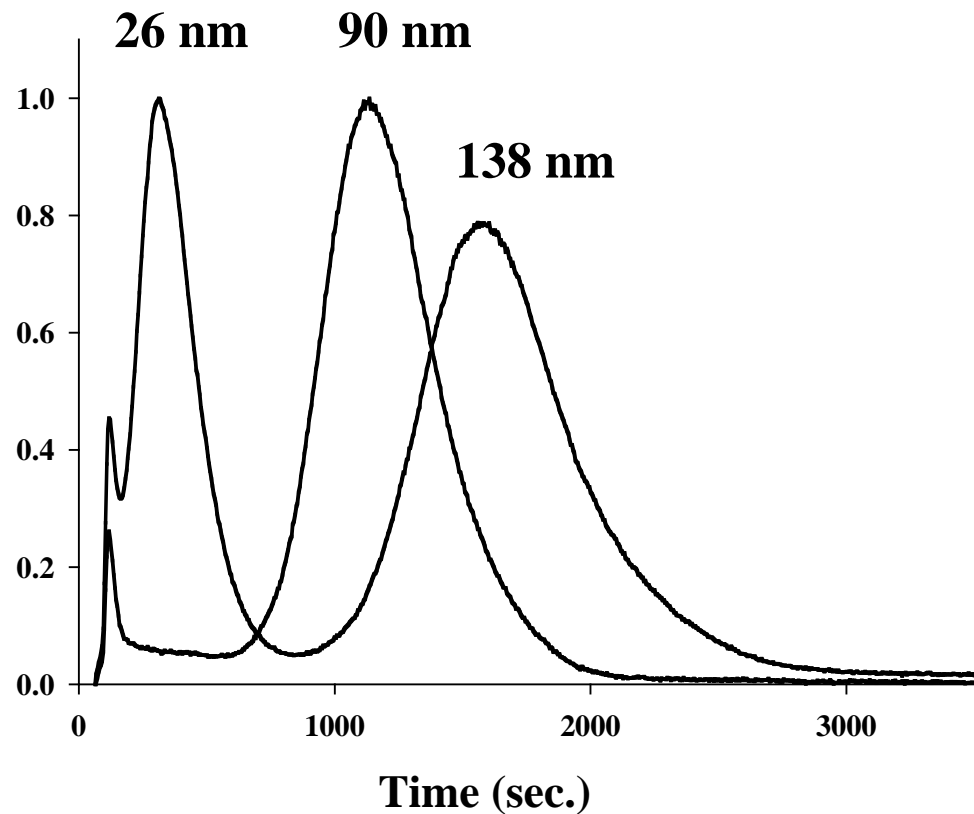
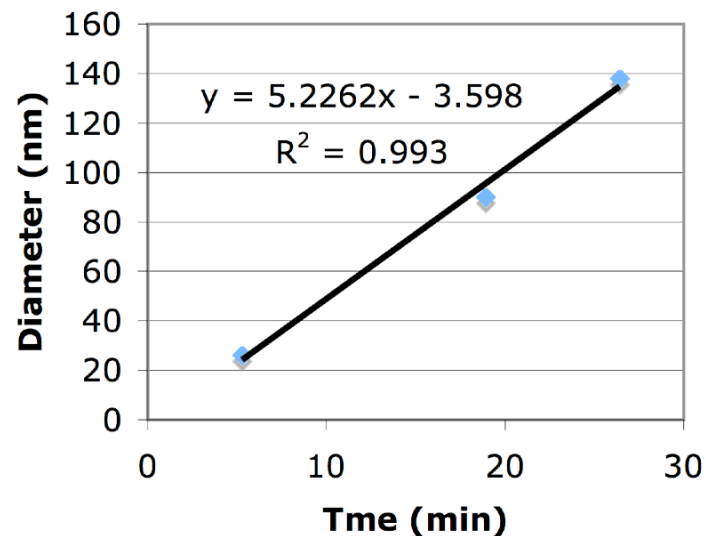


Separation of PSS molecular weight standards (Da)

High field: 3.0 ml/min Carrier flow: 1.0 ml/min

Low field for nanoparticles

- Low field: 0.9 ml/min
- Carrier flow: 1.0 ml/min
- PSS standards (Duke)
- 20 μL injection
- FI detector



Normal-Mode FFF Theory

Experimental Measurement

Computing d from retention time

$$R = \frac{t^0}{t_R}$$

t^0 = retention time for void volume
 t_r = retention time for sample component

FFF Theory

$$R = 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right]$$

$$\lambda = \frac{l}{w} = \frac{D}{Uw}$$

D = diffusion coefficient

U = field velocity

w = channel thickness (0.25 mm)

Stokes-Einstein

Sedimentation FFF

$$\lambda = \frac{6kT}{d^3 \pi \Delta \rho (\omega^2 r_o) w}$$

d = diameter

$\Delta \rho$ = density difference

ω = rpm

r_o = radius of centrifuge

Flow FFF

$$\lambda = \frac{DV^0}{V_c w^2} = \frac{kTV^0}{3\pi\eta V_c w^2 d}$$

V^0 = void volume

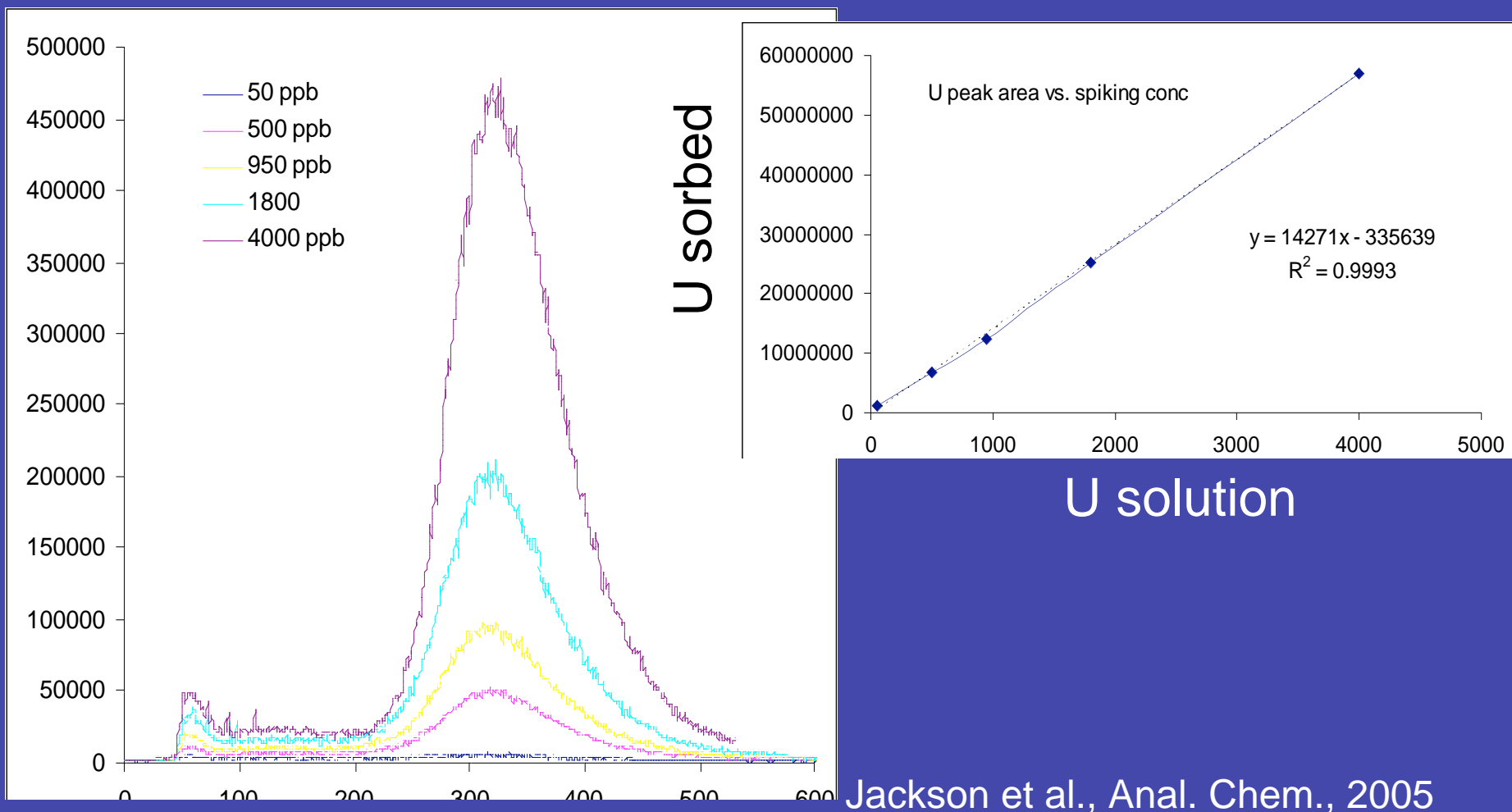
V_c = volumetric cross-flow rate

η = viscosity

Field flow fractionation: Uranium characterization applications

Laboratory Investigation of U(IV) Sorption to Bacteria

- Culture of *Shewanella oneidensis* ($\sim 10^6$ cells/mL)
- pH 5 linear isotherm by FFF-ICP-MS

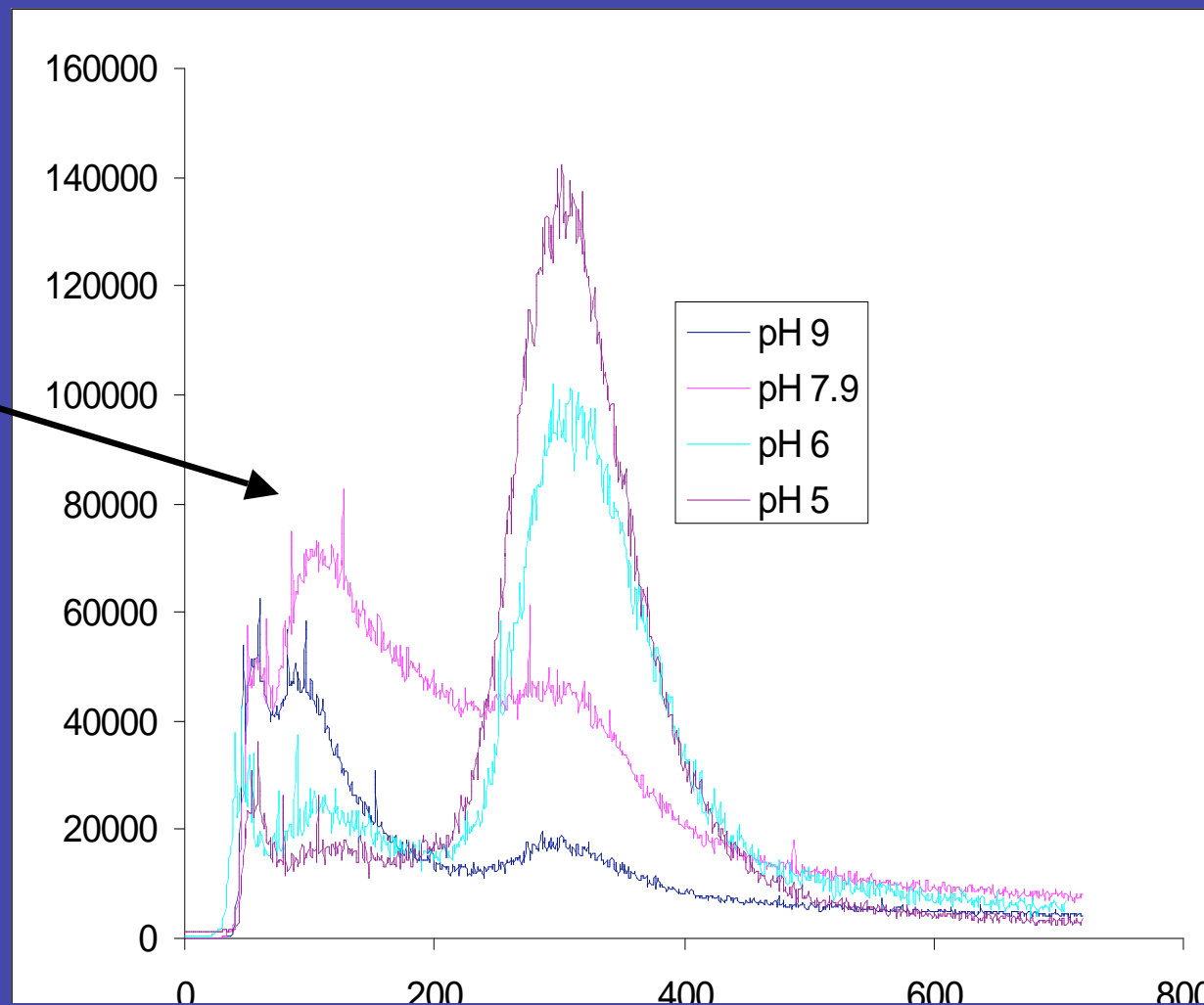


Jackson et al., Anal. Chem., 2005

Investigation of U Sorption to Bacteria

- pH dependence of sorption

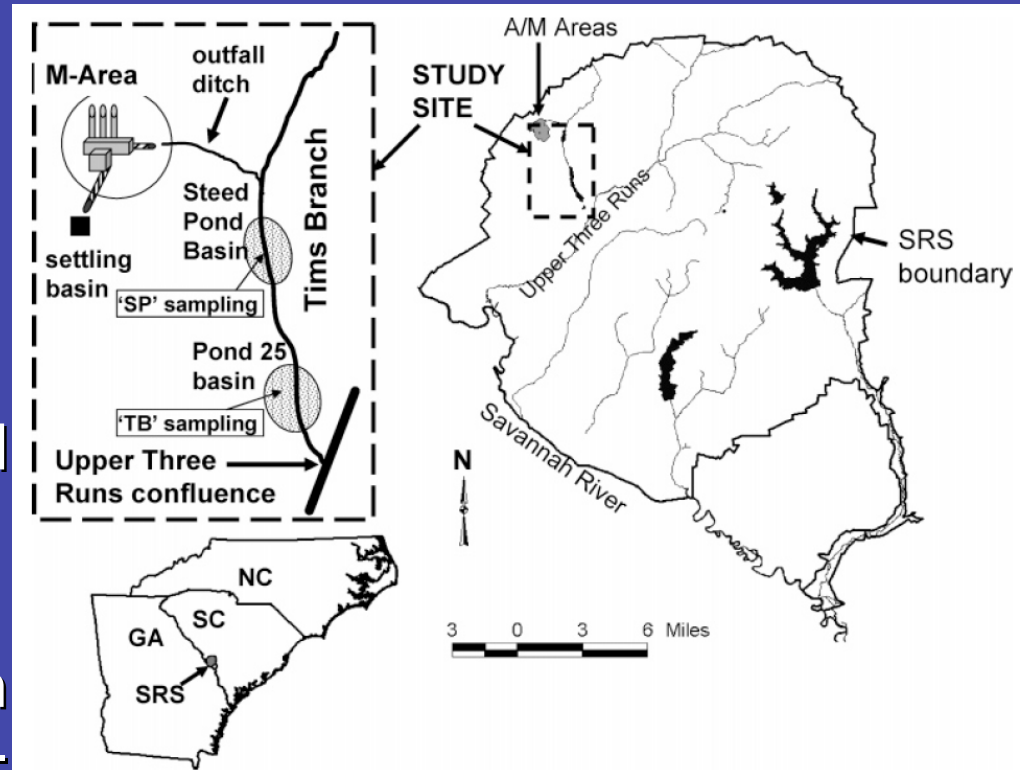
- Suspected high MW exopolymer competes with cells for U
- Proton competition is different for cells vs exopolymer
- FFF can be useful in studies of mixtures



Jackson et al., Anal. Chem., 2005

U and Ni porewater characterization at Savannah River Site, Aiken SC

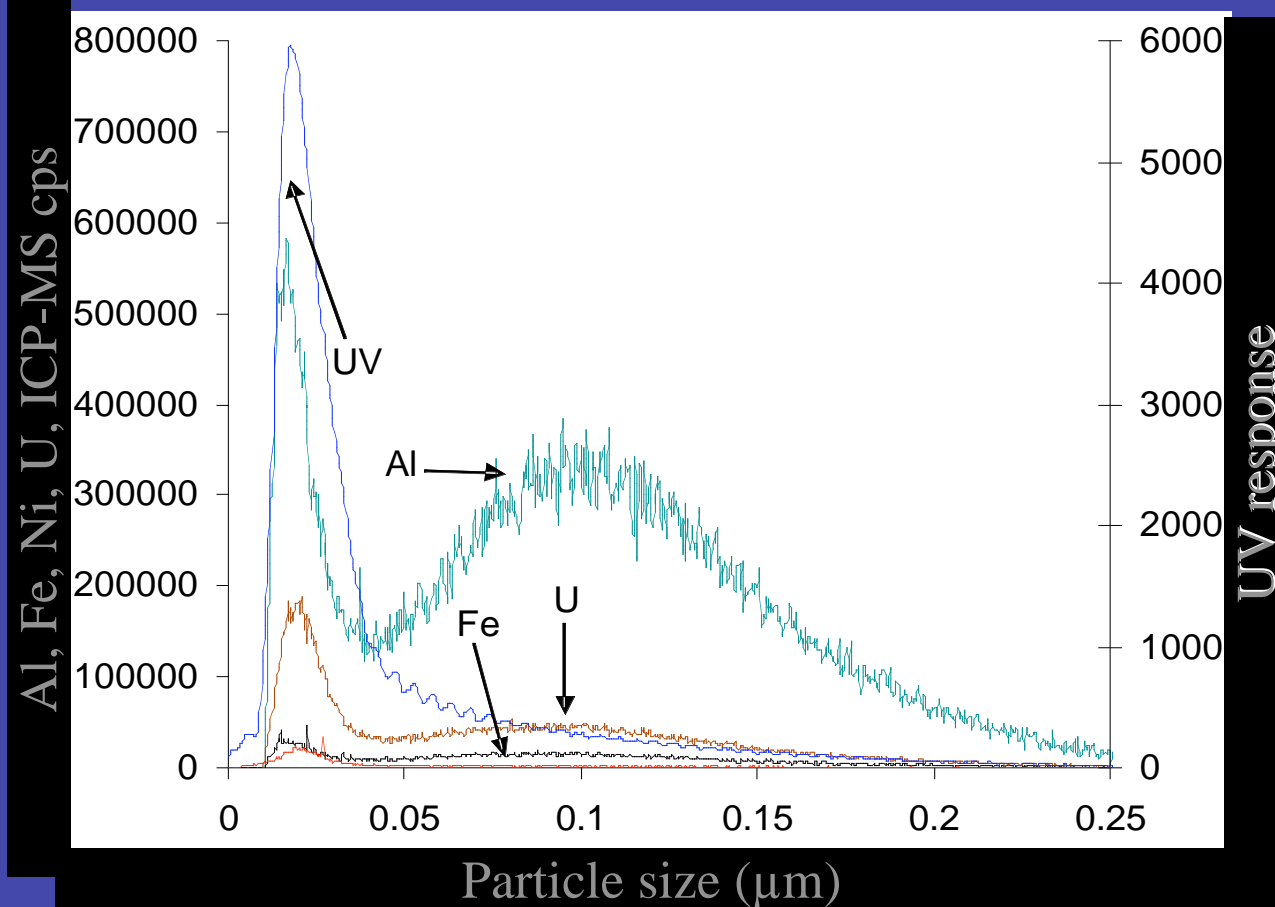
- Examined filtered ($0.2\ \mu\text{m}$) soil extracts (water-dispersible colloids) from SREL
- High levels of DOC suggest that metal-DOC binding might be important in Ni and U speciation
- Mildly acidic pH
- Interface FI-FFF on-line with ICP-MS for (multi-) element-specific chromatograms



SP5 water extract:

Sediment	pH	DOC (mg l ⁻¹)	Al (μg l ⁻¹)	Fe (μg l ⁻¹)	Ni (μg l ⁻¹)	U ((μg l ⁻¹)
SP5	5.94	200	4370	2060	407	237

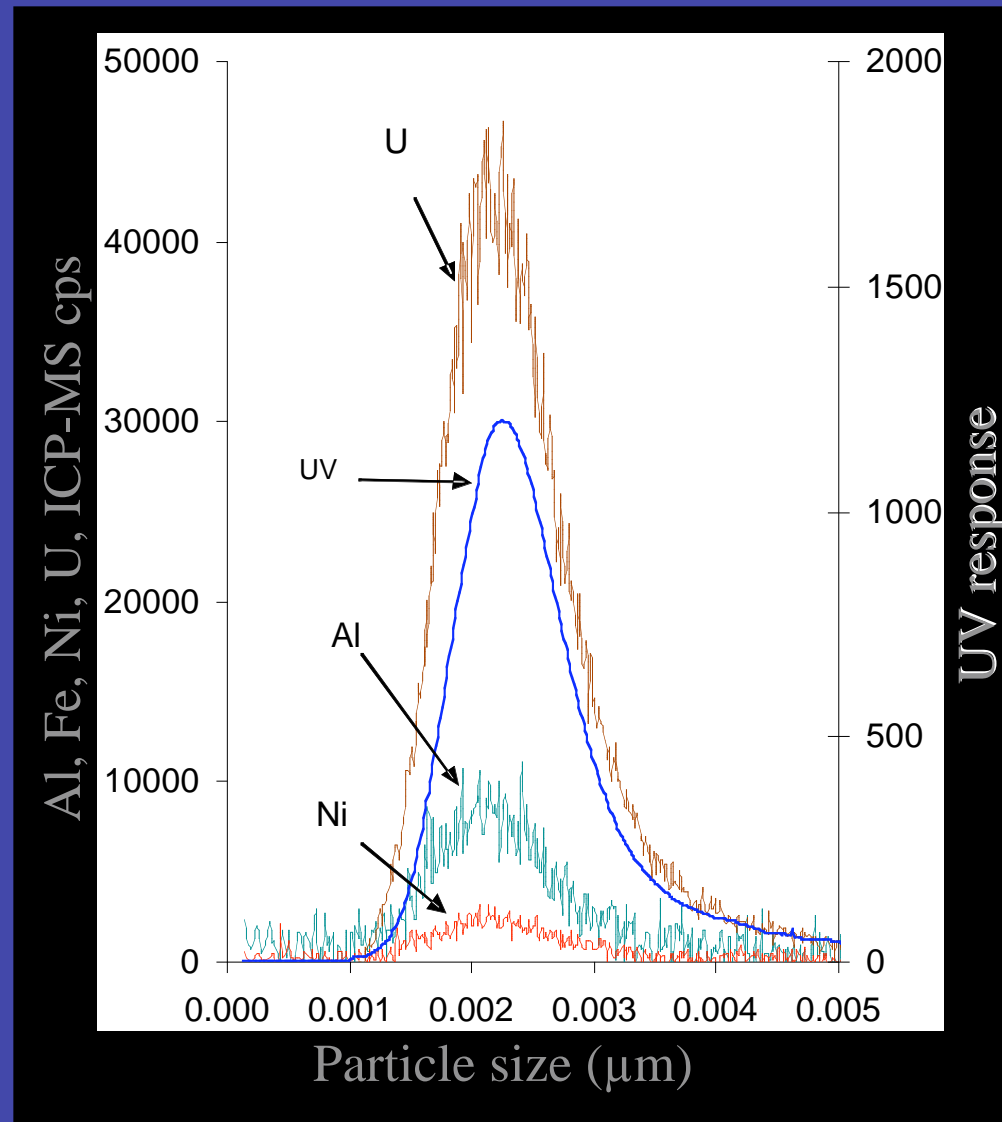
low field FI-FFF ICP-MS



Jackson et al., ES&T, 2005

SP5 water extract:

High Field FI FFF
ICP-MS



Jackson et al., ES&T, 2005

SREL Study Summary

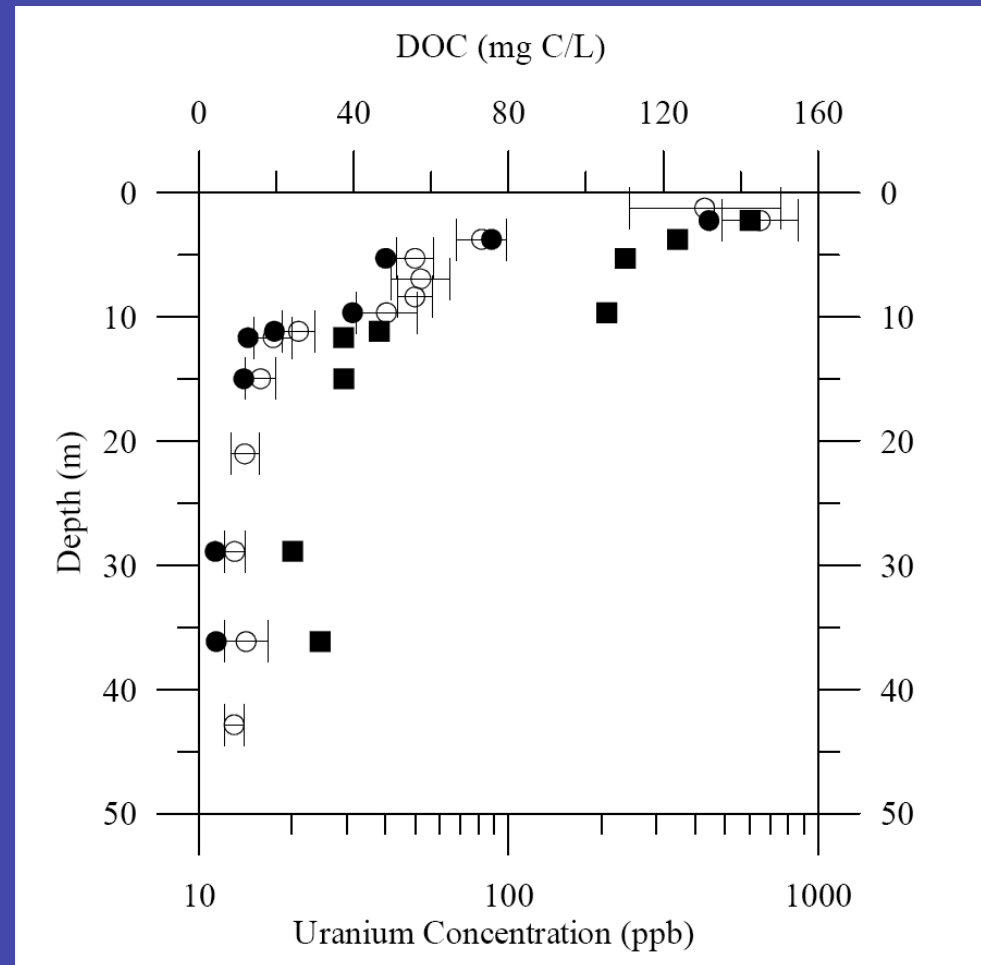
% U distribution

	U	SP1B1	SP2B1	SP5B1	TB6
SEC	Colloid	3.9	18.9	52.8	0.1
	Humic	29.4	26.8	22	21.8
FFF	Colloid	6.6	17.6	26.7	14.8
Low Field	Humic	38.4	20.3	17.3	30.5
High Field	Humic	22.6	9.1	9.6	12.4

- Environmental significance at SRS
 - ‘dissolved’ U may be partially non-available, associated with colloids and DOC
 - Soil/groundwater reactive transport models should include speciation

Compare to: Clay-rich glacial till aquitard

- Located in western Canada
- 80 m thick
- Mildly alkaline
- High in carbonate
- High in DOC
- Well-instrumented with peizometers
- Natural U source

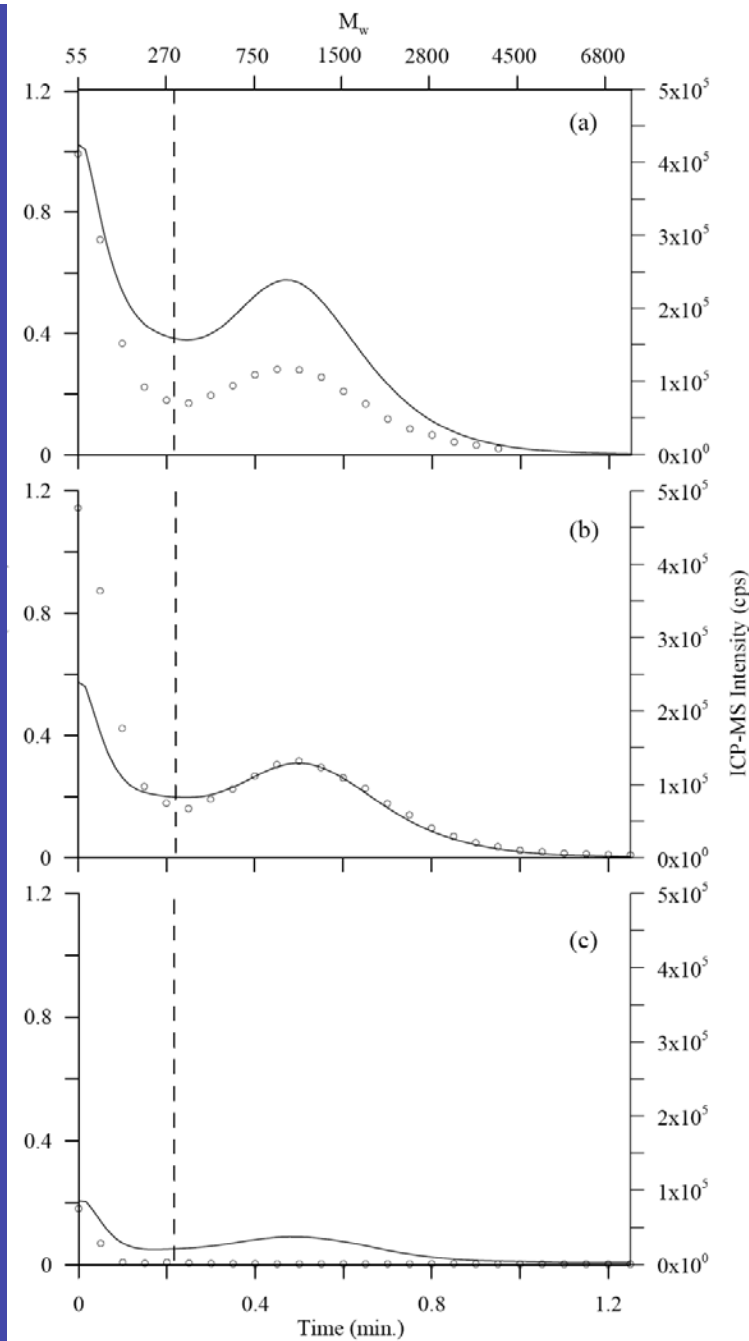


Ranville et al., J. Contam Hydrol, 2007

Depth = 2.3 m
 $U = 460 \mu\text{g/L}$
 $\text{DOC} = 136 \text{ mg/L}$

Depth = 4.5m
 $U = 430 \mu\text{g/L}$
 $\text{DOC} = 77 \text{ mg/L}$

Depth = 11.9 m
 $U = 38 \mu\text{g/L}$
 $\text{DOC} = 19 \text{ mg/L}$



Comparison of speciation model and FFF results

Water composition (mM)									
Ca	Mg	Na	K	Cl	SO ₄	CO ₃	U	DOC (mg/l)	pH
10	150	275	1.5	1.0	300	4.8	1.48E-3	77	7.6
Uranyl species percentage distribution									
Ca ₂ UO ₂ (CO ₃) ₃ ⁰		CaUO ₂ (CO ₃) ₃ ⁻		UO ₂ (CO ₃) ₂ ⁼		UO ₂ (CO ₃) ₃ ⁴⁻		-FA ₂ UO ₂	
66.2		2.2		0.8		28.9		1.9	

FFF results

- DOC was low in MW
- 50% recovery of DOC
- % Organic bound U measured = 0.62 %
- Assuming lost DOC contained U
 - 0.62 % x 2 = 1.24 %

Field flow fractionation

Quantitative applications

Why develop measurement methods when we have models?

- Are the models accurate for complex water compositions ?
 - Compare predictions to measurements
- What about complex ligands for which thermodynamic data are lacking?
 - Uncharacterized NOM
 - Natural nanoparticles
- Separation-based approach
 - Differentiation of “free” vs complexed
 - Mixtures
 - Competitive reactions (e.g. cells and mineral particles)
- Development begins with well-characterized ligands

U(VI) solution complexes can be predicted by computer modeling

- For example-Visual MINTEQ (Gustafsson, 2006)
- Uses thermodynamic data on uranium association with

Ligand	Dissolved	Colloidal
Inorganic	-OH, -CO ₃ , etc.	-FeOx surface sites
Organic	-acetate, -citrate, etc.	-fulvic acid, etc.

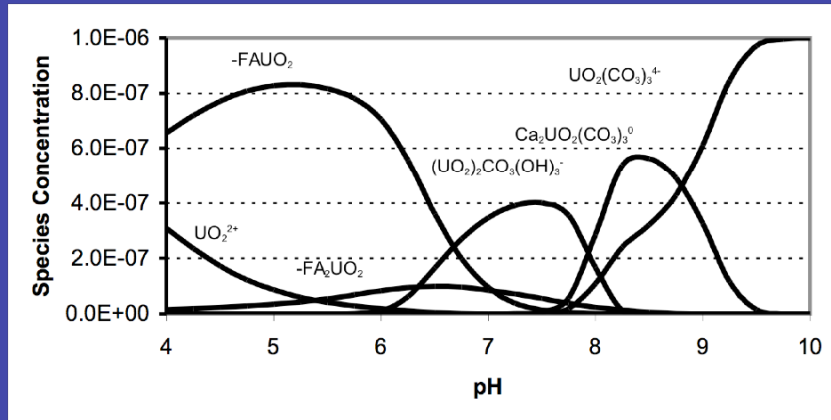
- Database likely “good” for complexes with dissolved inorganic and simple organic ligands (subject of new ERSP project: K. Hatfield PI)

U(VI) solution complexes predicted by computer modeling: DOC vs carbonate

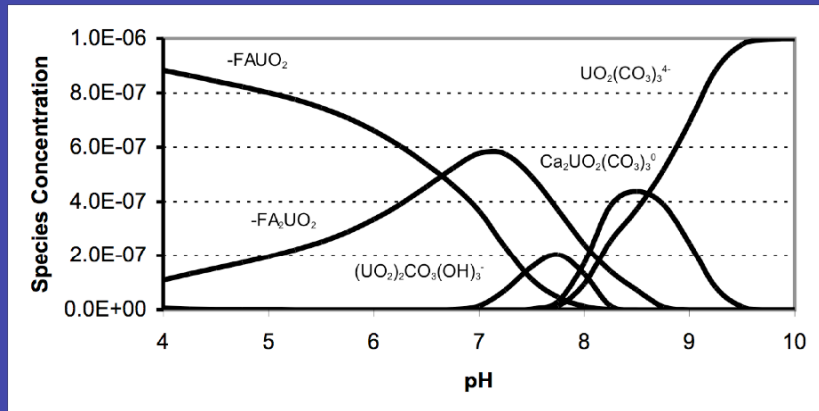
$U=10^{-6}$ M, DOC = 1 mg C/L

Increase organic complexes

$U=10^{-6}$ M, DOC = 10 mg C/L

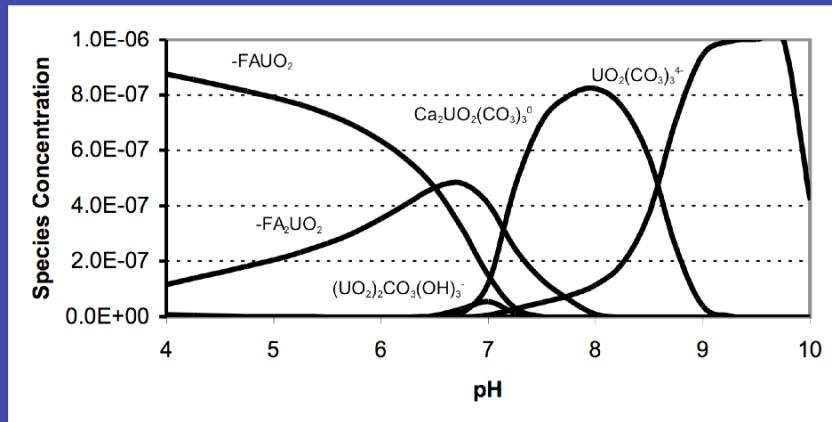


$Ca^{2+} = 10^{-3}$ M, atmospheric CO_2 ,



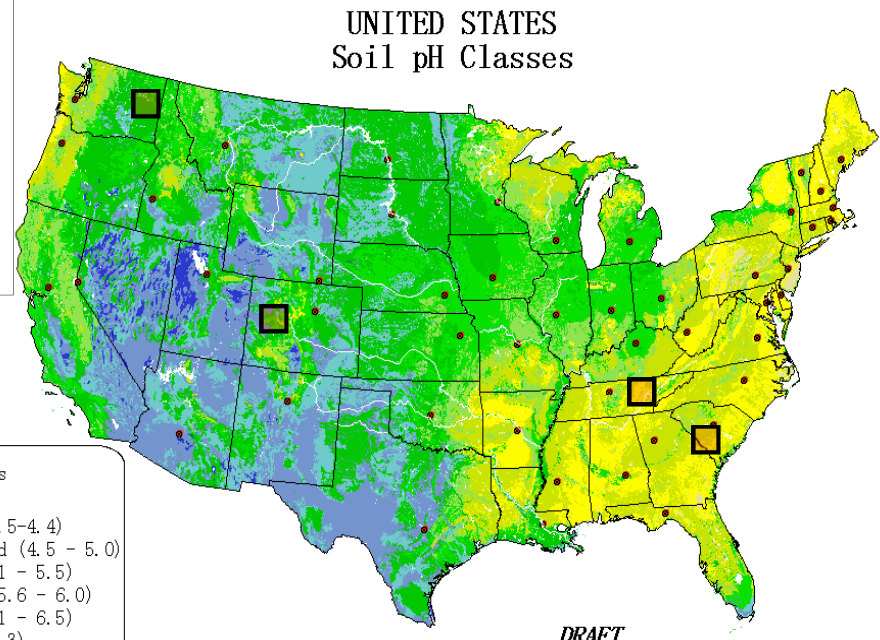
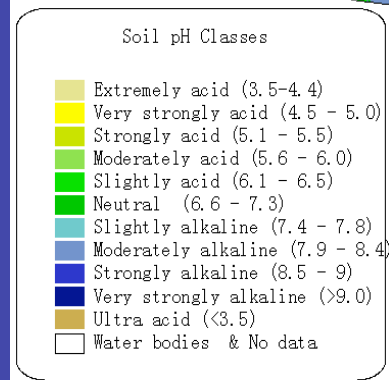
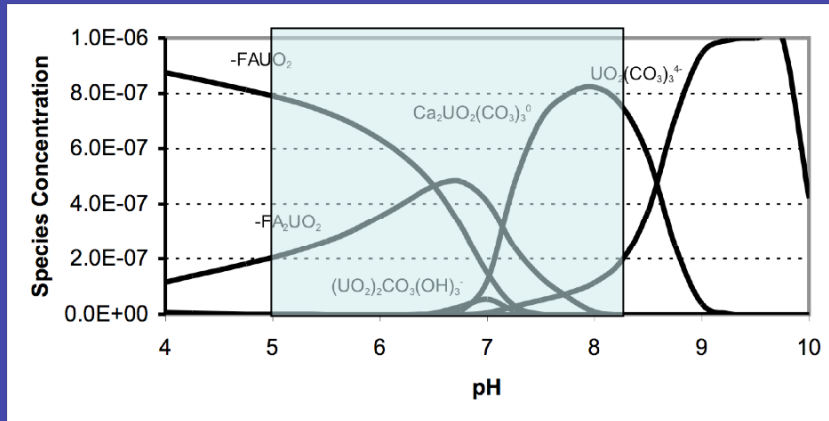
$Ca^{2+} = 10^{-3}$ M, atmospheric CO_2 ,

Decrease organic complexes



$Ca^{2+} = 2 \times 10^{-3}$ M, 10 X atmospheric CO_2 ,

U(VI) solution complexes predicted by computer modeling: Soil pH variations



100 0 100 Miles

Copyright (C) OSU Forage Program, 2001
Map Created by Soil and Fertilizer Institute, CAAS

Well-characterized ligand: Nanoparticulate Hematite

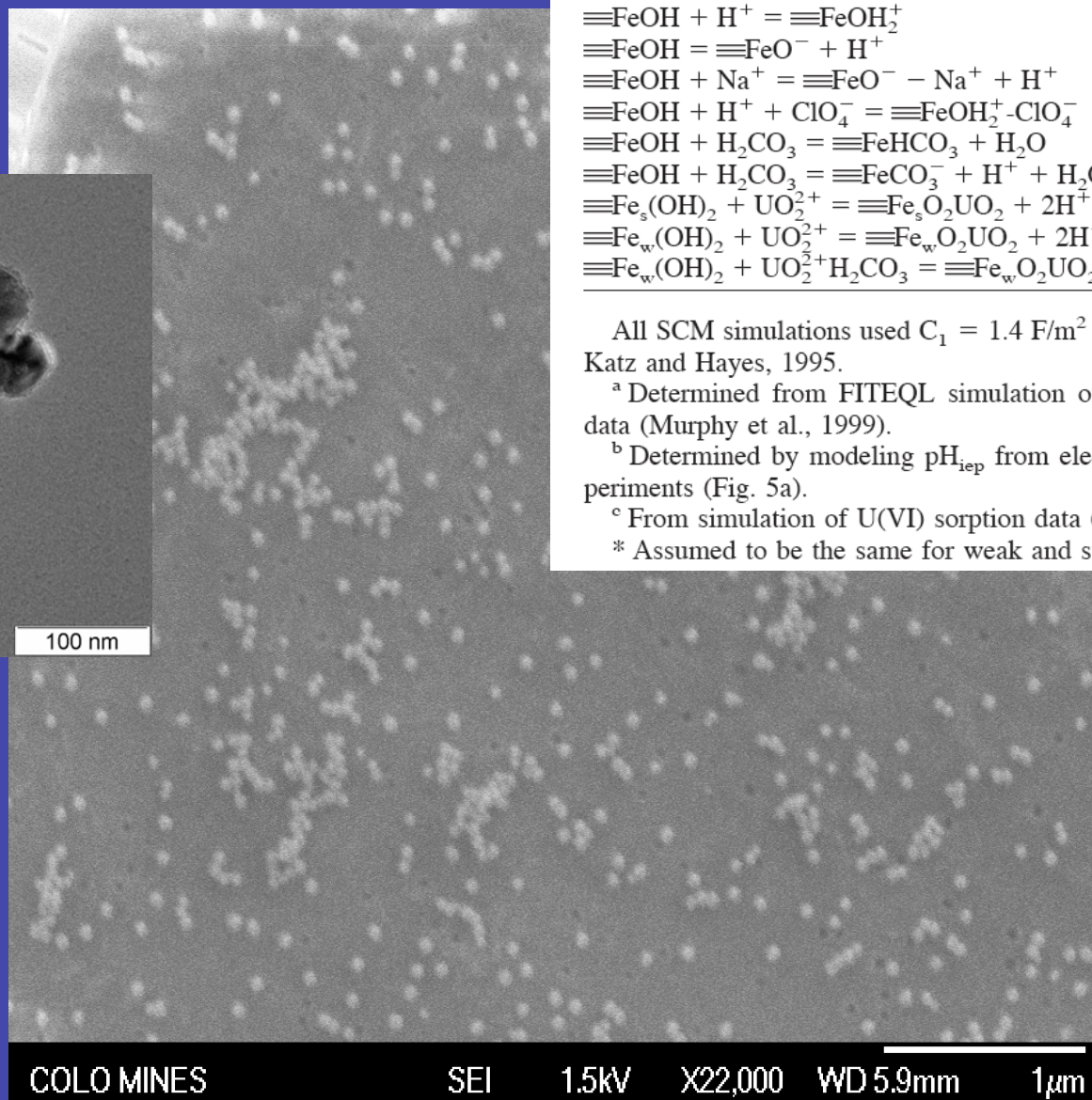
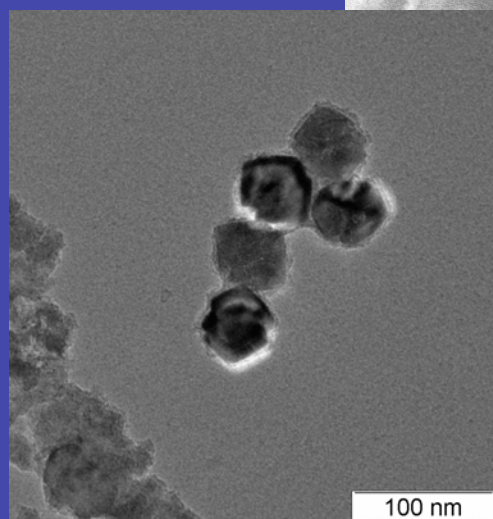


Table 3. Surface reactions.

Reaction	$\log K$ ($I = 0$)
$\equiv\text{FeOH} + \text{H}^+ = \equiv\text{FeOH}_2^+$	8.25 ^{a*}
$\equiv\text{FeOH} = \equiv\text{FeO}^- + \text{H}^+$	-10.25 ^{a*}
$\equiv\text{FeOH} + \text{Na}^+ = \equiv\text{FeO}^- - \text{Na}^+ + \text{H}^+$	-8.46 ^{a*}
$\equiv\text{FeOH} + \text{H}^+ + \text{ClO}_4^- = \equiv\text{FeOH}_2^+ - \text{ClO}_4^-$	10.18 ^{a*}
$\equiv\text{FeOH} + \text{H}_2\text{CO}_3 = \equiv\text{FeHCO}_3 + \text{H}_2\text{O}$	6.00 ^{b*}
$\equiv\text{FeOH} + \text{H}_2\text{CO}_3 = \equiv\text{FeCO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	-3.30 ^{b*}
$\equiv\text{Fe}_s(\text{OH})_2 + \text{UO}_2^{2+} = \equiv\text{Fe}_s\text{O}_2\text{UO}_2 + 2\text{H}^+$	-0.087 ^c
$\equiv\text{Fe}_w(\text{OH})_2 + \text{UO}_2^{2+} = \equiv\text{Fe}_w\text{O}_2\text{UO}_2 + 2\text{H}^+$	-3.43 ^c
$\equiv\text{Fe}_w(\text{OH})_2 + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 = \equiv\text{Fe}_w\text{O}_2\text{UO}_2\text{CO}_3^{2-} + 4\text{H}^+$	-12.14 ^{c*}

All SCM simulations used $C_1 = 1.4 \text{ F/m}^2$ and $C_2 = 0.2 \text{ F/m}^2$, after Katz and Hayes, 1995.

^a Determined from FITEQL simulation of potentiometric titration data (Murphy et al., 1999).

^b Determined by modeling pH_{iep} from electrophoretic mobility experiments (Fig. 5a).

^c From simulation of U(VI) sorption data (Figs. 1 and 2).

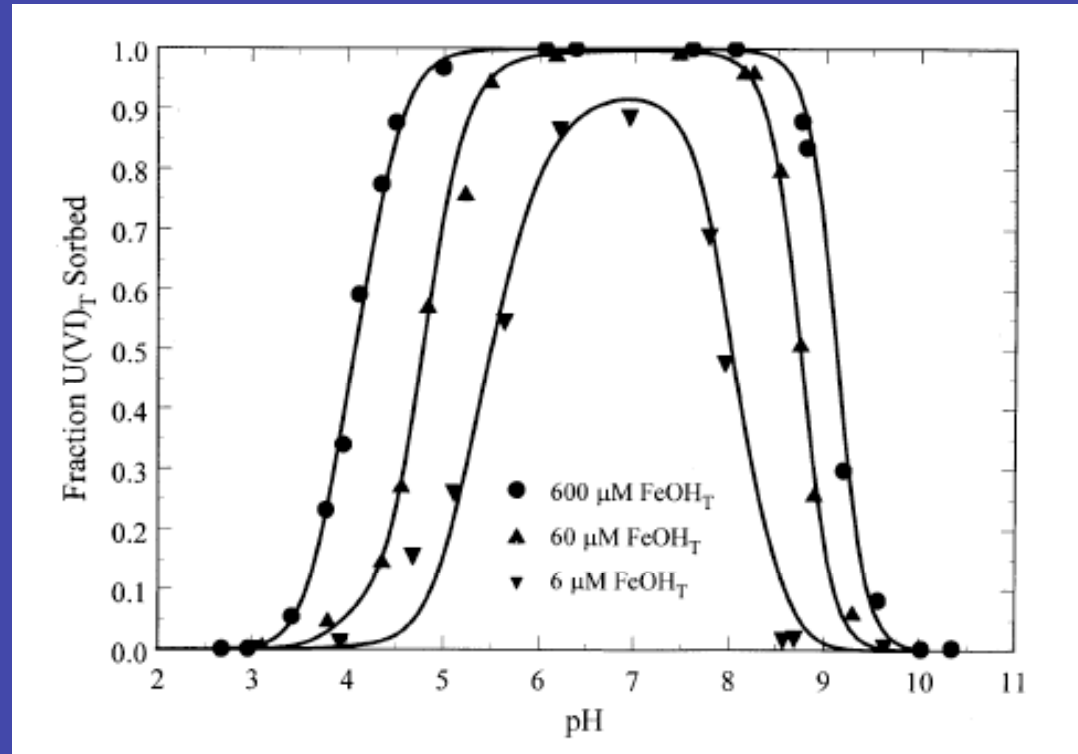
* Assumed to be the same for weak and strong site types.

Well-characterized
ligand:

Nanoparticulate
Hematite

Existing thermodynamic
surface complexation
sufficient to allow
predictions

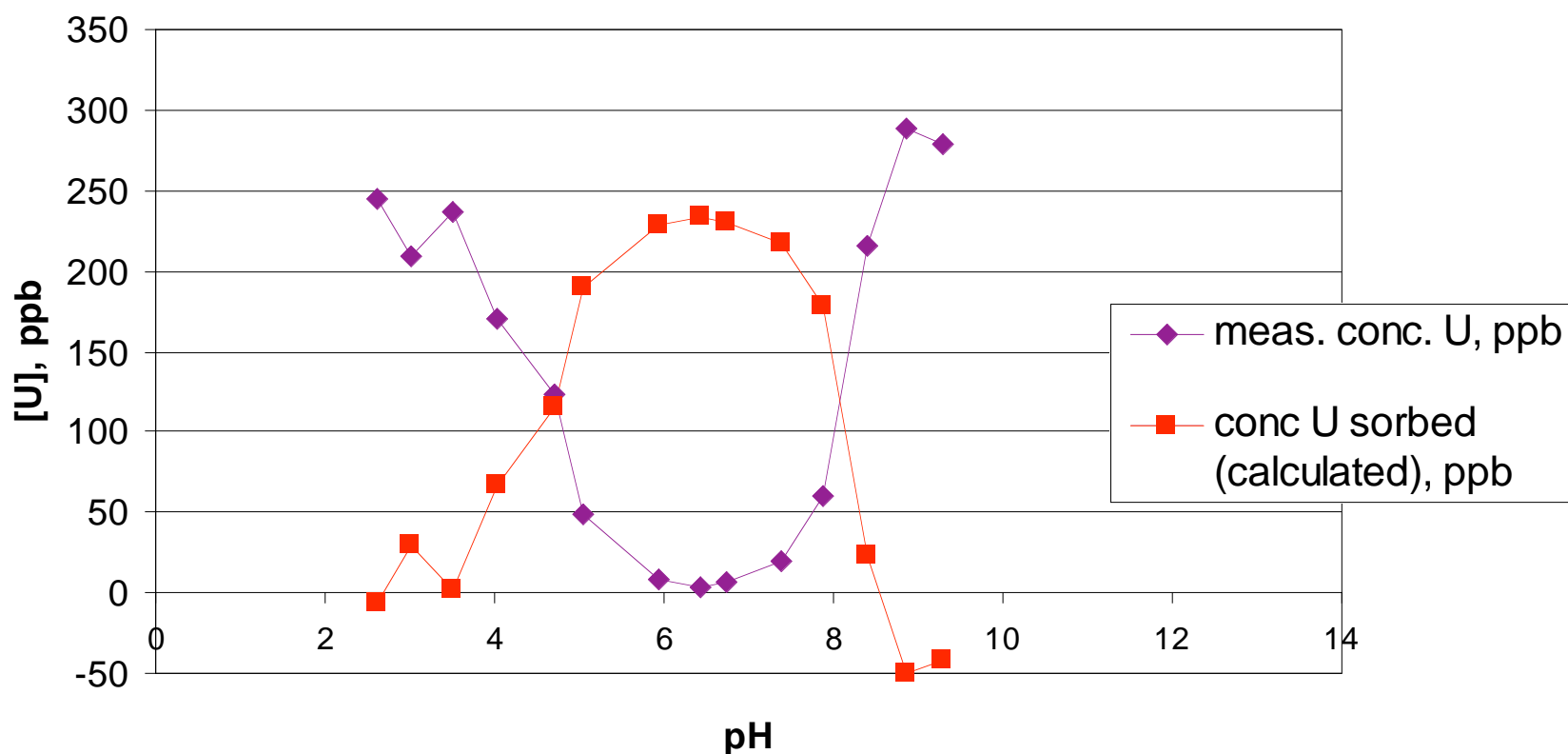
What about natural
nanoparticles ?



Experimental results and FITEQL model simulations of fraction uranium sorbed onto 0.09 g/l, 0.9 g/l and 9.0 g/l hematite at variable pH. Ionic strength = 0.1, $\text{U(VI)}_T = 10^{-6} \text{ M}$ and atmospheric concentrations of CO_2 . Lenhart and Honeyman (1999).

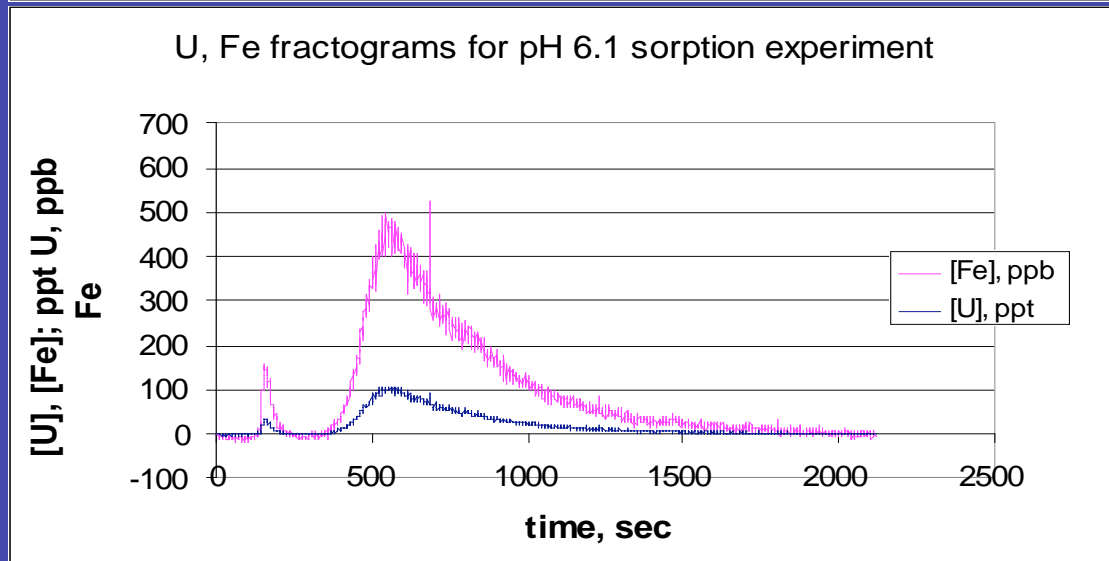
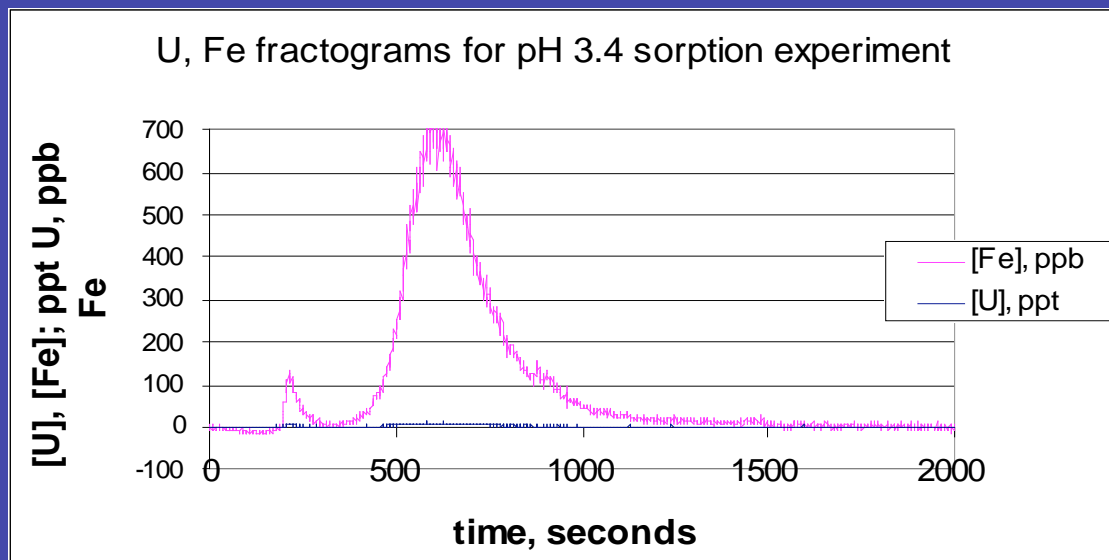
Batch Sorption Experiments

Uranium sorption onto hematite: [hematite]=0.09 g/L, [U]=1 μ M (238 ppb), I=0.1 M, atmospheric CO₂

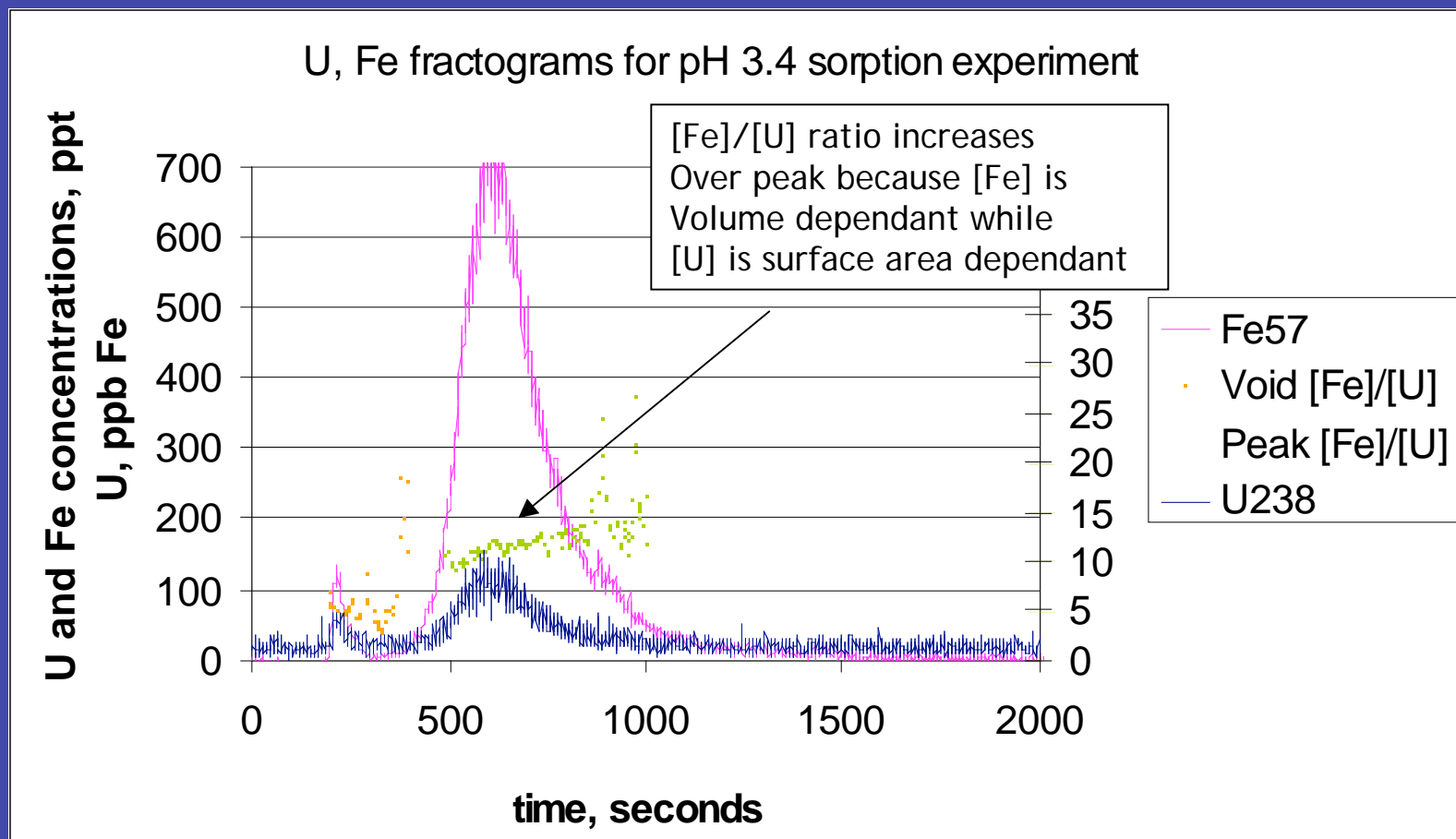


Phase separation using filtration
Volume for ICP-MS ~10 ml

Sorption Experiment: FI FFF-ICP-MS

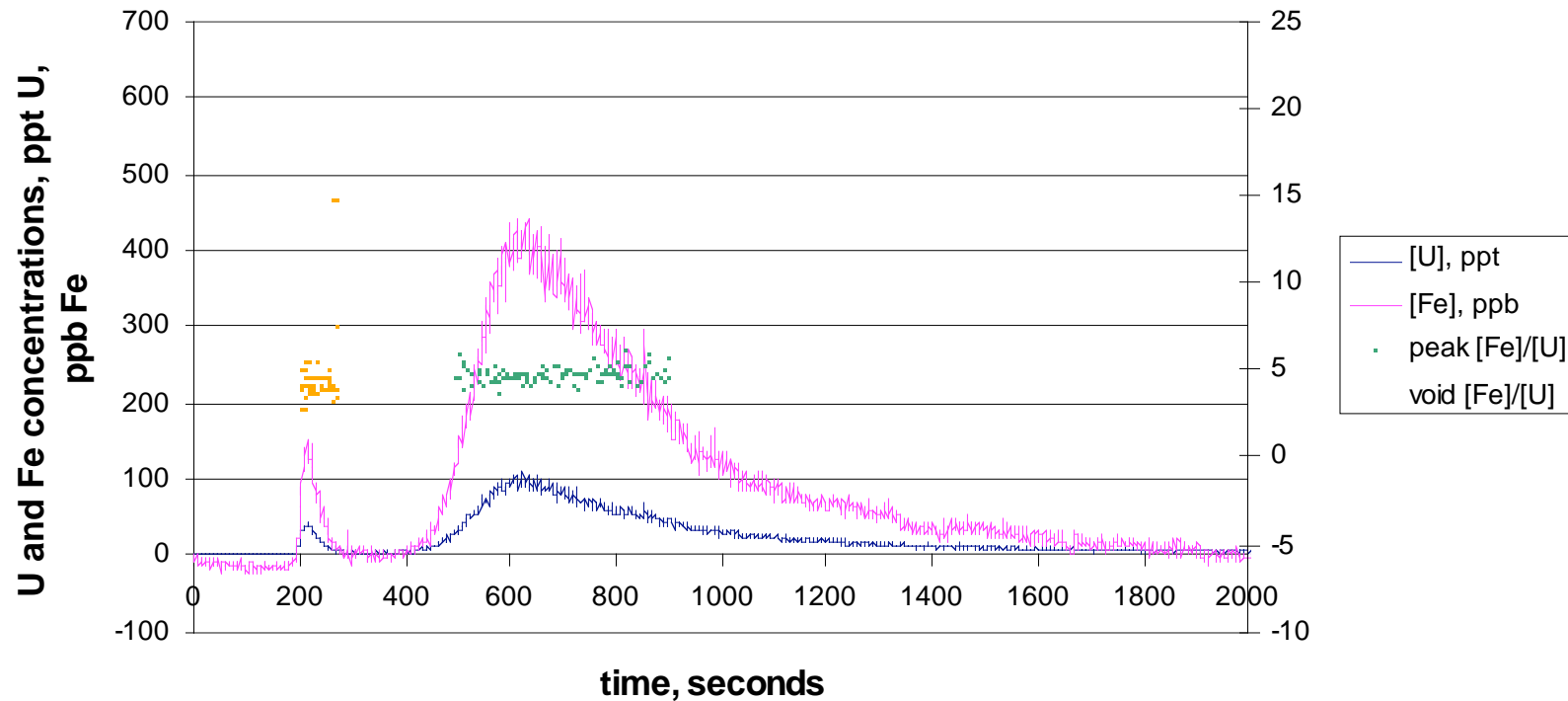


20 μ L injected into FI FFF-ICP-MS



- Smaller $[Fe]/[U]$ ratio in void peak. Indicates some dissolved U.
- Increasing $[Fe]/[U]$ ratio over peak. Function of sorbed [U] being surface area dependant, [Fe] being volume dependant

U, Fe fractograms for pH 5.3 sorption experiment



- Void peak ratio close to peak ratio, indicates U present in hematite that was not fully injected/equilibrated

Comparison of sorption results: FFF vs batch

	FFF		Filtered: aqueous analysis	
pH	% Sorbed	Log Kd	% Sorbed	Log Kd
3.4	4.5	1.7	5.1	1.8
4.2	58.4	3.2	29.2	2.7
4.2	50.4	3.1	29.2	2.7
5.3	96.1	4.4	99.1	5.1
6.1	100	5.3	99.6	5.4

Future Work

- Method Validation
 - Complete Hematite work
 - Examine IHSS HA
- Up-scaled Lab Experiments
 - Construct small tank with layered heterogeneous materials
 - Carbonate, organic matter
 - Sample at high spatial resolution, utilizing the small sample volume requirements of FFF-ICP-MS to examine U speciation
- Field-scale
 - Examine U speciation at field sites (part of new ERSP project)

Funding



Acknowledgements

DOE ERSP Grant: ER64419
Edna Bailey Sussman Fellowship



Student Investigators



Emily Leshar: Poster S4: Optimization of Flow-Field Flow Fractionation-Inductively Coupled Plasma Mass Spectrometry for U(VI) Characterization



Ph.D. Opportunities

The Colorado School of Mines has a program of National Need Graduate Fellowships for students pursuing a Ph.D. in areas of environmental science and engineering. Students will participate in co-

Contact:
Linda Figueroa
Lfigueroa@mines.edu

Research program has funding for Graduate Assistantships in Areas of National Need. Opportunities to students pursuing a Ph.D. in areas of environmental science and engineering. Students will also participate in co-

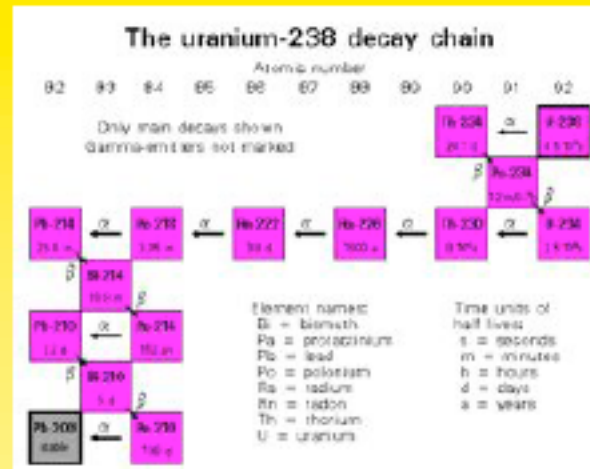
Benefits:

- * Annual stipend of up to \$30,000
- * Payment of tuition and fees
- * Conference travel allowance

This program is open only to U.S. citizens and permanent resident aliens studying at a U.S. university.

This is an equal opportunity program and is open to all qualified persons without regard to race, sex, creed, age, physical disability or national origin.

Applications are due by February 15, 2008.

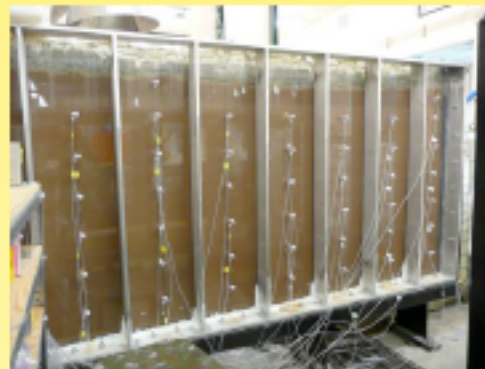


Microbial uranium immobilization

Graduate Programs:
 Chemistry & Geochemistry
 Environmental Science & Engineering

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Updated 12/21/07



Tank-scale studies of uranium transport



Field Sampling Campaign in Naturita, CO (former uranium mill site)